

Equations of state for liquid helium

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With 5 figures in the text

1. It is a remarkable fact that helium in the liquid state has values of the atomic heat capacity smaller than the value $3R/2$ characteristic of mono-atomic gases while already the next inert gas, neon, and other elements in the liquid state have heat capacities well above the value $3R$ characteristic of solids. This suggests the conception of liquid helium as a condensed gas whereas other liquids are best described as highly disordered crystals. The wellknown attempts to describe liquid He^4 as a condensed Bose-Einstein gas have not been very successful quantitatively. In the following we shall discuss the consequences of a treatment of liquid He^4 and He^3 as condensed highly degenerate states of a Fermi gas. The results are in both cases remarkably positive, which is rather surprising as He^4 with zero resulting spin is not expected to obey the Fermi statistics in the usual state of gas.

2. **Equations for a condensed Fermi gas at constant volume.**—We shall first present the equations given by Fermi (1) for a highly degenerate gas at constant volume and transform them to suit our purpose of discussing the gas as condensed. The specific heat C , the entropy S , the energy E and the free energy F pro mole at sufficiently low temperatures T are given by

$$C = \gamma T \quad (1)$$

$$S = \gamma T \quad (2)$$

$$E = E_0 + \frac{\gamma}{2} T^2 \quad (3)$$

$$F = E_0 - \frac{\gamma}{2} T^2 \quad (4)$$

where γ is a constant that can be obtained from experiment, and E_0 is the zero-point energy. The four equations (1) to (4) are thermodynamically connected. The pressure of the gas is obtained by Fermi by the use of the virial theorem which, in connection with equation (3), gives

$$P = \frac{2}{3} \frac{E}{V} = \frac{2}{3} \frac{E_0}{V} + \frac{1}{3} \frac{\gamma}{V} T^2 \quad (5)$$

where V is the mole volume.

We can express the parameters γ and E_0 as functions of V and the atomic weight A .

The theoretical expression for γ is

$$\gamma = N \frac{\pi^2 k^2 m}{h^2} \left(\frac{4\pi g}{3n} \right)^{\frac{2}{3}} \quad (6)$$

where N is the number of atoms per mole, k the Boltzmann constant and h the Planck constant. For a gas like He^4 the factor g is unity and the mass m is the product of the atomic weight A and the physical mass unit m_1 , that is

$$g = 1 \quad \text{and} \quad m = A m_1. \quad (7)$$

For a condensed gas the number n of atoms per unit of volume has to be replaced by

$$n = \frac{N}{V - b} = \frac{N}{\beta} \quad (8)$$

where V is the total volume pro mole, and b corresponds to the b of van der Waals equation and represents the volume occupied by the apparently rigid cores of the atoms. β thus is the volume at disposal for the movement of the atoms and corresponds to what the present writer (2) has called the volume parameter. Inserting (7) and (8) in (6) we obtain

$$\gamma = \pi^2 \left(\frac{4\pi}{3} \right)^{\frac{2}{3}} \frac{N^{\frac{1}{3}} k^2 m_1}{h^2} A \beta^{\frac{2}{3}} = 0.1563 A \beta^{\frac{2}{3}} \frac{\text{Joule}}{\text{mole deg}^2} \quad (9)$$

if β is given cm^3/mole . From the experimental values of γ we can by this formula obtain β . If our working hypothesis is right β has to come out smaller than the mole volume V but of the same order of magnitude.

The zero-point energy E_0 is given by

$$E_0 = N \frac{3}{10} \frac{h^2}{m} \left(\frac{3n}{4\pi g} \right)^{\frac{2}{3}} \quad (10)$$

or with respect to (7) and (8)

$$E_0 = \frac{3}{10} \left(\frac{3}{4\pi} \right)^{\frac{2}{3}} \frac{N^{\frac{5}{3}} h^2}{m_1} \frac{1}{A \beta^{\frac{2}{3}}} = 1310 \frac{1}{A \beta^{\frac{2}{3}}} \frac{\text{Joule}}{\text{mole}} \quad (11)$$

if β is in cm^3/mole .

The total pressure of the Fermi gas when condensed to liquid is a sum of the external pressure p and a second part which is compensated by the attracting forces between the atoms. In another connection the present writer (2) has called this part the pressure parameter α . Inserting $P = p + \alpha$ in equation (5) using the expressions (9) and (11) for γ and E_0 , and transforming from Joule/cm^3 to atmospheres by the factor 9.872 we obtain

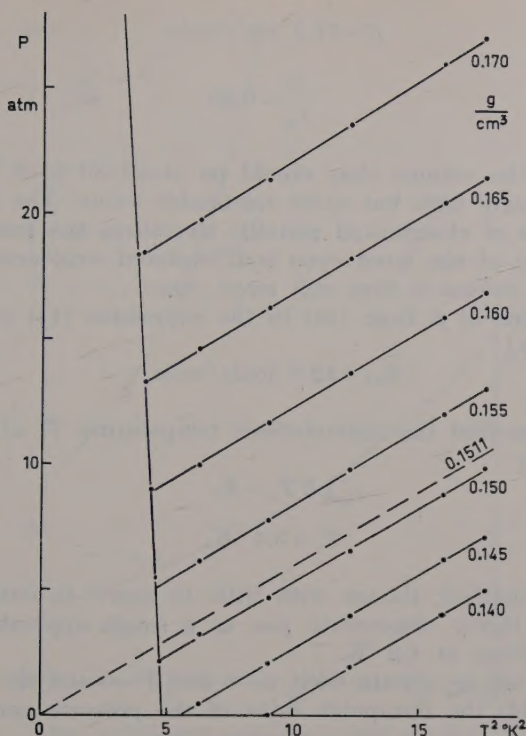


Fig. 1. Isopycnals of He I.

$$p + \alpha = 8625 \frac{1}{V A \beta^{\frac{2}{3}}} + 0.5144 \frac{A \beta^{\frac{2}{3}}}{V} T^2 \text{ atm} \quad (12)$$

where V and $\beta = V - b$ are in cm^3/mole . This is to a first approximation a $p - V - T$ equation of state of the liquid, which, however, has to be completed by the determination of the volume dependence of α .

3. The isopycnals of He I.—The extensive measurements of Keesom and Miss Keesom (3) on the pressure-volume-temperature relationship in liquid helium give a first possibility to test the applicability of the Fermi-gas theory. Figure 1 shows some of the isopycnals, which were given by Keesom and Keesom in a $p - T$ diagram, transformed by means of the tabulated data into a $p - T^2$ diagram. In accordance with equation (12) the plots for constant densities and volumes in this diagram appear as straight lines.

In this series of lines the dashed one, which goes through the origin, corresponds to the density 0.1511 g/cm^3 and to the mole volume of He I for $T = 0$ and $p = 0$

$$V_{0I} = 26.5 \text{ cm}^3/\text{mole}. \quad (13)$$

The slope of the dashed line is 0.595 atm/deg^2 . It gives by means of equation (12) with $A = 4.00$

$$\beta = 21.2 \text{ cm}^3/\text{mole} \quad (14)$$

$$\text{and} \quad \frac{\beta}{V_0} = 0.80. \quad (15)$$

The free part of the volume thus should be about 80 % of the total volume, which is a surprisingly high but quite reasonable value. The free, compressible part of the volume of closepacked metallic structures has been found (2, 4) to be about 20 %, and of the more open body-centered structures about 40 %. The structure of liquid helium is thus still more open.

Inserting the value of β from (14) in the expression (11) we obtain the zero-point energy of He I

$$E_{0I} = 42.6 \text{ joule/mole}. \quad (16)$$

Using this value we find the characteristic temperature T_c of the Fermi theory which is defined by

$$\frac{3}{2} R T_c = E_0 \quad (17)$$

$$\text{to be} \quad T_c = 3.4 \text{ }^\circ\text{K}. \quad (18)$$

We therefore are justified, though with little to spare, in our use of equations (1) to (5) for a highly degenerate gas as a rough approximation up to the boiling point of helium at 4.2 °K.

From equation (12) we obtain with $p=0$ and $T=0$ and the values of V_{0I} and β from (13) and (14) the zero-point value of the pressure parameter α

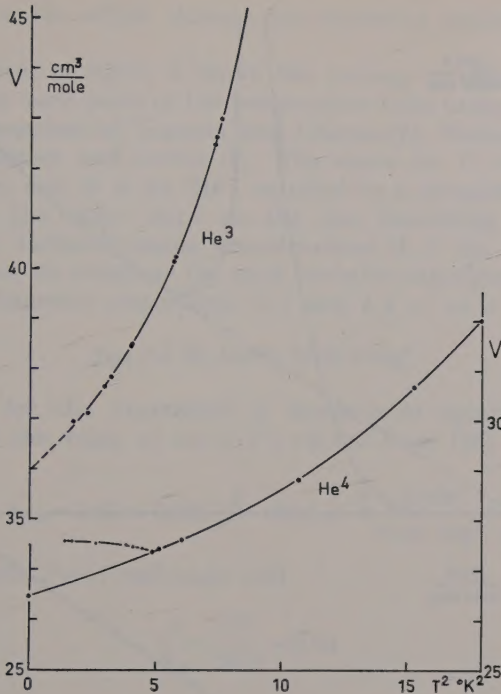
$$\alpha_0 = 10.3 \text{ atm}. \quad (19)$$

4. The thermal expansion of liquid helium and its influence on calorimetric data.—In the following sections 5 and 6 we intend to compare for He⁴ and He³ the results from measurements of the specific heat C , the energy E and the entropy S with the theory. These measurements are made, however, not at constant volume but at the pressure of the saturated vapour, which means an appreciable thermal change of volume. It is therefore necessary first to consider the thermal expansion and its influence on the calorimetric results.

In figure 2 we have plotted the atomic volumes of He⁴ and He³, computed from density measurements of Onnes and Boks (5) respectively Kerr (6), against the square of the absolute temperature. In the case of He⁴ I the direct determinations in the range from 2.4 to 4.2 °K are completed by the zero-point value V_{0I} of the volume from (13). We see that the initial change of volume is proportional to T^2 , just as the initial change of energy. The initial proportionality between the changes of volume and energy found by Grüneisen is thus valid also for helium. The initial slopes give, if b in equation (8) is assumed to be constant,

$$\frac{dV}{d(T^2)} = \frac{d\beta}{d(T^2)} = 0.185 \frac{\text{cm}^3}{\text{mole deg}^2} \text{ for He}^4 \text{ I} \quad (20)$$

$$\text{and} \quad \frac{dV}{d(T^2)} = \frac{d\beta}{d(T^2)} = 0.50 \frac{\text{cm}^3}{\text{mole deg}^2} \text{ for He}^3. \quad (21)$$


 Fig. 2. Thermal expansion of He⁴ and He³.

The influence of the thermal expansion on the atomic heat capacity C as work against the vapour pressure is rather small, at most of the order of 0.1 Joule/mole $\times$ deg near the boiling point, and will be disregarded.

The influence caused by a change of the zero-point energy is more pronounced and has to be considered. Equations (3), (9), and (11) give for the energy

$$E = 0.07815 A \beta^{\frac{2}{3}} T^2 + 1310 \frac{1}{A \beta^{\frac{2}{3}}}. \quad (22)$$

Derivating with respect to T and omitting terms of higher order than T we obtain the atomic heat capacity.

$$C = \frac{dE}{dT} = \left[0.1563 A \beta^{\frac{2}{3}} - 1310 \frac{4}{3} \frac{d\beta}{d(T^2)} \frac{\beta^{-\frac{5}{3}}}{A} \right] \times T \frac{\text{Joule}}{\text{mole deg}}. \quad (23)$$

C thus is still approximately proportional to T but appreciably smaller than the proportionality factor γ at constant volume which corresponds to the first term in (23). The second term is of the order of 20 % of the first one.

Equation (23) with the initial slopes from figure 2 inserted for $d\beta/d(T^2)$ is a first approximation for the lowest temperatures. There is, however, an appreciable increase of the slopes with increasing temperature already below the boiling points which apparently depends on the fact that the critical points,

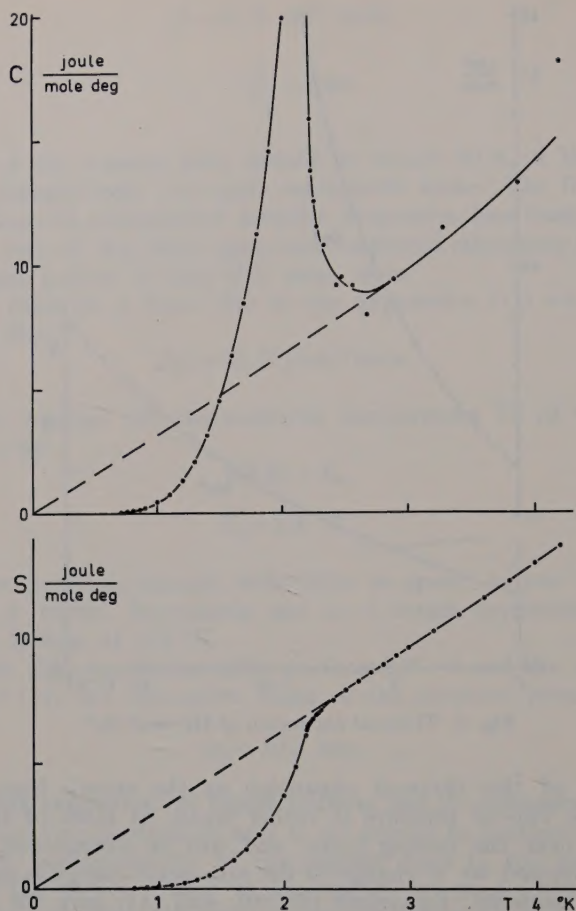


Fig. 3. Atomic heat capacity C and entropy S at the pressure of the saturated vapour.

where the slopes have to be vertical, are very near to the boiling points. The critical point of He^4 is 5.4°K and of He^3 3.4°K . Our approximation therefore is a very rough one.

5. Specific heat and entropy of He^4I .—The upper diagram in figure 3 shows the atomic heat capacity C of liquid helium as a function of the temperature. We are here mainly interested in the part of the curve between the λ -transition and the boiling point, that is, in the range from 2.4 to 4.2°K . Unfortunately this range has not been investigated as thoroughly as the range below and around the λ -point. There seems to be just one series of measurements published by Keesom and Clusius in 1932 (7). These measurements give the specific heat of helium under the pressure of its saturated vapour. The corrections for the work against the external pressure are smaller than the accidental errors of the measurements. Within the limits of errors it is possible to draw

a straight line from the origin through the measuring points, in accordance with equation (23).

The lower diagram of figure 3 shows the entropy S obtained by integrating over C/T from the zero point of the temperature scale using experimental values for C from measurements of Keesom and Clusius (7), Keesom and Keesom (8), and Kramers, Wasscher and Gorter (9). The scales for C and S are the same, Joule/mole $\times$ degree, and S is for He I satisfied by a straight line from the origin which has nearly the same slope as the line describing C . This is as could be expected from thermodynamic considerations if C for He I is proportional to T . For the slopes we obtain as the most probable experimental values from the upper and lower diagrams respectively 3.7 and 3.4 or as a mean value

$$\gamma_{\text{sat}} = 3.55 \text{ Joule/mole} \times \text{deg}^2. \quad (24)$$

Here γ_{sat} stands for the expression in brackets in equation (23) which with $A=4.00$ and with the value of $d\beta/d(T^2)=0.185$ from (20) gives

$$\gamma_{\text{sat}} = 3.55 = 0.625 \beta^{\frac{2}{3}} - 80.5 \beta^{-\frac{5}{3}} \frac{\text{Joule}}{\text{mole deg}^2}. \quad (25)$$

From (25) we obtain $\beta = 17 \text{ cm}^3/\text{mole}$ and

$$\frac{\beta}{V_0} = \frac{17}{26.5} = 0.64. \quad (26)$$

This value is of the right order but 20 % smaller than the probably more accurate value 0.80 obtained in section 3 from the p - V - T measurements. The difference is possibly due to the fact that in the range of He I the V - T^2 curve in figure 2 has a slope that appreciably exceeds the initial slope $0.185 \text{ cm}^3/\text{deg}^2$ used in our calculations. A less rough approximation will probably reduce the difference.

6. The entropy of He^3 .—As far as is known at present the isotope He^3 as condensed does not have a transition into a superfluid state. On the other hand the thermal properties are complicated by the alignment of the nuclear spins. In figure 4 we have plotted the results obtained by Roberts and Sydoriak (10) for the entropy S in Joule/mole $\times$ degree against the temperature T . The upper curve gives the total entropy and the lower the part of it due to the thermal motions of the atoms. Disregarding the fact that this line does not exactly point towards the origin, which may well be due to the difficulties of the measurements and of the separation of the two parts, the entropy is expressed by

$$S = 3.50 T \frac{\text{Joule}}{\text{mole deg}}. \quad (27)$$

With S thus proportional to T we have $C=S$ and obtain with $A=3.00$ and $d\beta/dT^2=0.50$ (from 21) and considering that $g=2$ for He^3

$$3.50 = 0.745 \beta^{\frac{2}{3}} - 183 \beta^{-\frac{5}{3}}, \quad (28)$$

which gives $\beta = 17.5$ and

$$\frac{\beta}{V_0} = \frac{17.5}{36} = 0.49. \quad (29)$$

A better approximation would probably give a higher value.

7. Consequences concerning He II.—The thermal properties of pure He II are mainly known from the measurements of the specific heat below 0.6°K by Kramers, Wasscher and Gorter (9). Above this temperature the picture is complicated by the beginning of the transition into He I. Below 0.6°K the atomic heat capacity is by these authors given as

$$C_{\text{II}} = (0.094 \pm 0.006) \cdot T^3 \text{ Joule/mole} \times \text{deg}. \quad (30)$$

This gives for the energy

$$E_{\text{II}} = E_{0\text{II}} + \frac{0.094}{4} T^4 \text{ Joule/mole} \quad (31)$$

and for the free energy

$$F_{\text{II}} = E_{0\text{II}} - \frac{0.094}{12} T^4 \text{ Joule/mole}. \quad (32)$$

The experimental heat capacity was found to be in good agreement with a modified Debye theory for longitudinal waves only, so that the number of vibrational degrees of freedom is N per mole, instead of $3N$ in the Debye theory. We may write the atomic heat capacity

$$C = N \frac{4\pi^4 k}{5\theta^3} T^3 \quad (33)$$

and obtain from (30) the characteristic temperature

$$\theta = 15.2^\circ\text{K}. \quad (34)$$

In figure 5 the thermal properties of He II are confronted with the thermal properties of He I on the assumption that the latter obey the laws of a degenerate Fermi gas. The ordinate is energy with the energy of He II at $T=0$ as origin. The abscissa is T^2 .

The extrapolated curve for the free energy F_{II} of He II calculated from (32) give rather small deviation from the zero line in the range of temperature up to the boiling point at 4.2°K . The energy of the liquid in equilibrium in the range of transition and of He I above this range are obtained by integration of the specific heat data from measurements of Keesom and Clusius (7), Keesom and Keesom (8), and Kramers, Wasscher and Gorter (9). Above the transition range the energy of He I in the chosen diagram according to equation (23) gives a straight line which extended to the axis gives the difference of the zero-point energies for He I and He II

$$E_{0\text{I}} - E_{0\text{II}} = 5.5 \text{ Joule/mole}. \quad (35)$$

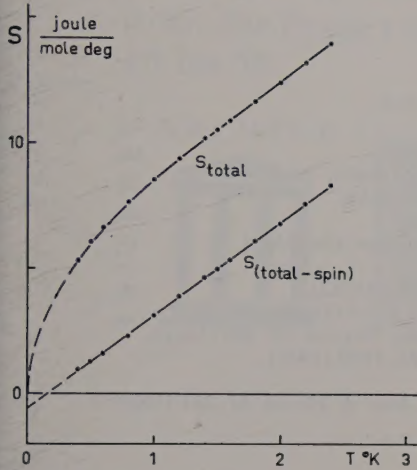


Fig. 4. Total entropy of He³ and the part of it due to the movements of the atoms.

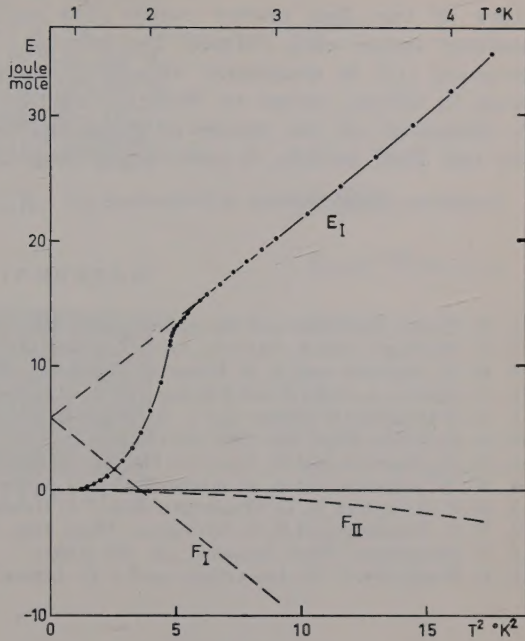


Fig. 5. Energy and free energy of He⁴ versus T^2 .

From this and the calculated value (16) of the zero-point energy of He I we now obtain the zero-point energy of He II as

$$E_{0\text{II}} = 42.6 - 5.5 = 37.1 \text{ Joule/mole.} \quad (36)$$

According to the modified Debye expression for He II this zero-point energy should be given by

$$E_{0\text{II}} = f \frac{N k \theta}{2} \quad (37)$$

where f is a factor depending on the frequency distribution of the phonon spectrum, which in the simple theory of Debye, assuming a distribution of modes proportional to the square of the frequencies, is 0.75. Our values for $E_{0\text{II}}$ from (36) and for θ from (34) gives

$$f = 0.58. \quad (38)$$

The free energy F_I of He I is according to equation (4) given in figure 5 by a straight line from the same origin as that of the energy E and with a slope of the same size as that of the energy but with negative sign. This line cuts the curve for the free energy F_{II} of He II at about $T = 1.9^\circ \text{K}$ in the range of the λ -transition. The fact that the two curves cut at a finite angle means, as is nowadays well recognized, that the observed smooth transition does not, as was once proposed by Ehrenfest (11), depend on an accidental contact of higher

order of two free energy curves but on the possibility of a series of intermediate states with reduced free energy. This interpretation, which was first proposed (12) in connection with the discovery of the order-disorder transformations in alloys, seems to hold for all now known transitions of higher order. A discussion of the nature of these intermediate states for He^4 , described by the two fluid models, is outside the scope of the present paper.

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